



Atmosphere Resource Recovery and Environmental Monitoring Trace Contaminant Control Through FY 2012

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TABLE OF CONTENTS

1. BACKGROUND AND TECHNOLOGY DESCRIPTION	1
1.1 Carbon Bed Assembly	1
1.2 Catalytic Oxidizer Assembly	2
1.3 Sorbent Bed Assembly	2
1.4 Opportunities for International Space Station Trace Contaminant Control System Improvement	2
2. PROGRESS: PLANNED, ACTUAL, AND RESULTS	3
2.1 Fixed Bed	3
2.2 High-Temperature Catalytic Oxidizer	4
2.3 Orion Trace Contaminant Control Bed	4
2.4 Heat Melt Compactor Contaminant Control System	5
3. FUTURE WORK	7
3.1 Orion Trace Contaminant Control Bed	7
3.2 High Flow Rate Carbon Bed	7
3.3 Orion Smoke Eater	7
3.4 Photocatalytic Oxidation System	7
3.5 Sorbent Testing and Evaluation	8
APPENDIX A—BENCH-SCALE CHARACTERIZATION OF CANDIDATE SORBENTS AND CATALYSTS (TRACE CONTAMINANT CONTROL: CARBON DIOXIDE AND WATER REMOVAL)	9
A.1 Overview—Candidate Sorbent and Catalyst Testing by Kennedy Space Center	9
A.2 Silicalite	9
A.3 Immobilized Amines (G10 and Polyethyleneimine-Silane)	10
A.4 Low-Temperature Carbon Monoxide Catalysts	11
A.5 Honeywell Photocatalyst Evaluation	12
APPENDIX B—BENCH-SCALE DEVELOPMENT OF A CATALYST FOR SELECTIVE CONVERSION OF AMMONIA TO NITROGEN	15
B.1 Summary	15
B.2 Synthesis of a Low-Temperature, Platinum-Based Catalyst for Ammonia Removal	16
B.3 Study of Ammonia Removal Using Closed-Loop Fourier Transform Infrared Spectrometer	18

TABLE OF CONTENTS (Continued)

B.4 Low-Temperature, Platinum-Based Catalyst Testing	20
B.5 Future Development of Low-Temperature, Platinum-Based Catalyst	23
REFERENCES	25

LIST OF FIGURES

1.	XPS analysis of TDA Research catalyst before and after an ethanol challenge: (a) New and (b) used	12
2.	LTP catalyst samples	17
3.	RVCS block diagram	18
4.	Custom gaseous NH_3 generator	19
5.	RVCS chamber NH_3 concentration dynamic	20
6.	RVCS chamber NH_3 concentration decay profile	21
7.	Temperature influence on N_2O concentration in the RVCS chamber	22

LIST OF TABLES

1.	Event timeline for Honeywell PCO catalyst testing	13
2.	NH ₃ removal rate corrected for RVCS chamber leakage	22

LIST OF ABBREVIATIONS, ACRONYMS, AND SYMBOLS

ARC	Ames Research Center
ARREM	Atmosphere Resource Recovery and Environmental Monitoring
ARS	atmosphere revitalization system
CBA	carbon bed assembly
CCS	contaminant control system
CDRA	carbon dioxide removal assembly
CO	carbon monoxide
CO ₂	carbon dioxide
COA	catalytic oxidizer assembly
E-chamber	exploration chamber
FF PCO	fast flow photocatalytic oxidation
FTIR	Fourier transform infrared
FY	fiscal year
GC	gas chromatograph
GCMS	gas chromatograph mass spectrometer
H ₂ O	water
HMC	heat melt compactor
HTCO	high-temperature catalytic oxidizer
ISS	International Space Station
KSC	Kennedy Space Center

LIST OF ABBREVIATIONS, ACRONYMS, AND SYMBOLS (Continued)

LiOH	lithium hydroxide
LTP catalyst	low-temperature, platinum-based catalyst
MSFC	Marshall Space Flight Center
N ₂	nitrogen
N ₂ O	nitrous oxide
NaOH	sodium hydroxide
NETL	National Energy Technology Laboratory
NH ₃	ammonia
NH ₄ Cl	ammonium chloride
NO	nitric oxide
NO _x	nitrogen oxide
NO ₂	nitrogen dioxide
PCI	Precision Combustion, Inc.
PCO	photocatalytic oxidation
PEI	polyethyleneimine
Pt	platinum
RVCS	regenerable volatile organic compound control system
rNH ₃	ammonia removal rate corrected for chamber leak rate
SBA	sorbent bed assembly
SCO	selective catalytic oxidation

LIST OF ABBREVIATIONS, ACRONYMS, AND SYMBOLS (Continued)

TCC	trace contaminant control
TCCS	trace contaminant control system
TRL	Technology Readiness Level
UOP	Universal Oil Products
UV	ultraviolet
UVA	ultraviolet A
UVC	ultraviolet C
V-chamber	vacuum chamber
VOC	volatile organic compound
XPS	x-ray photoelectron spectroscopy

TECHNICAL MEMORANDUM

ATMOSPHERE RESOURCE RECOVERY AND ENVIRONMENTAL MONITORING TRACE CONTAMINANT CONTROL THROUGH FY 2012

1. BACKGROUND AND TECHNOLOGY DESCRIPTION

This Technical Memorandum presents the results of work accomplished during fiscal year (FY) 2012 for the Advanced Exploration Systems Atmosphere Resource Recovery and Environmental Monitoring (ARREM) project in the trace contaminant control (TCC) functional area.

TCC has been a concern of spacecraft designers and operators from early in the progression of manned spaceflight. Significant technological advancement has occurred since the first designs were implemented in the 1960s, culminating in the trace contaminant control system (TCCS) currently in use aboard the International Space Station (ISS) as part of the atmosphere revitalization system (ARS).

Within the ARS, the TCCS can be considered an independent system. The TCCS draws inlet air directly from the cabin through a port in the face of its rack and exhausts treated air out into the cabin via a dedicated outlet within the rack. The system was designed for 5.25 crew persons, and due to its parallel operation with a similar Russian system, provides ample contaminant elimination capability to the ISS.

The TCCS consists of three primary subsystems: (1) The carbon bed assembly (CBA), (2) the catalytic oxidizer assembly (COA), and (3) the sorbent bed assembly (SBA).

1.1 Carbon Bed Assembly

The CBA is a 24-in-long bed filled with 22.7 kg (50 lb) of Barnebey-Sutcliffe® Type 3032 coconut shell activated carbon treated with phosphoric acid 10% by weight. The CBA is responsible for purifying the cabin air of most large molecular weight chemical compounds and ammonia (NH₃). The CBA accomplishes the bulk of contaminant removal by means of physical adsorption, a process in which compounds are entrapped by angstrom-sized pores on a material surface. The CBA removes NH₃ from the cabin air, and the phosphoric acid impregnation on the carbon accomplishes this through chemical adsorption.

1.2 Catalytic Oxidizer Assembly

The COA consists of a recuperative heat exchanger, a heating element, and a catalytic reactor. The catalytic reactor is filled with 0.5 kg of 0.5% palladium on alumina pellets and operates at a mean temperature of 400 °C. Incoming air is heated to reactor operating temperatures by the recuperative heat exchanger and heating element, and the reactor exhaust is cooled in the recuperative heat exchanger prior to entering the final subsystem.

1.3 Sorbent Bed Assembly

The SBA consists of a single bed filled with 1.4 kg of lithium hydroxide (LiOH) pellets. The purpose of the SBA is to prevent any acid gases that are generated in the catalytic reactor from escaping into the cabin atmosphere. The SBA accomplishes acid gas removal through chemical adsorption.

1.4 Opportunities for International Space Station Trace Contaminant Control System Improvement

For the ARREM TCC task, several advancements to these legacy technologies were pursued and utilized in FY 2012. First, a new activated carbon was required to fill the role of the CBA due to the discontinuation of the Barnebey-Sutcliffe Type 3032 product. Equivalent or upgraded capability was sought via commercially available products.

Similarly, FY 2012 efforts sought to eliminate the need for the SBA. The LiOH pellets in the SBA are known to degrade during operation and cause pressure drop increases in the TCCS. Chemical adsorbent media alternatives to LiOH were sought in the pursuit of an option that would preserve pressure drop characteristics throughout bed operation.

Thirdly, TCC task efforts sought to utilize an upgrade to the traditional pelletized COA reactor. Built by Precision Combustion, Inc. (PCI) for NASA as a Small Business Innovative Research (SBIR) phase II in the mid-2000s, the ultra-short channel Microlith[®] reactor supplants the original pelletized bed with a tightly spaced matrix of conductive material coated in catalyst. Previous testing of this unit has shown that light-off time (time elapsed between system activation and system efficacy) is greatly reduced compared to the legacy reactor.

2. PROGRESS: PLANNED, ACTUAL, AND RESULTS

FY 2012 accomplishments for the ARREM TCC task can be aligned with five areas of focus: (1) The fixed bed, (2) the high-temperature catalytic oxidizer (HTCO), (3) the Orion TCC bed, (4) the heat melt compactor (HMC) contaminant control system (CCS), and (5) sorbent and catalyst evaluation.

2.1 Fixed Bed

Planned progress for the fixed bed began with identifying a suitable replacement for the sorbent in the ISS TCCS CBA, Barnebey-Sutcliffe Type 3032, coconut shell activated carbon; calculating the contaminant capacity of the fixed bed given the new sorbent's bulk density and the conditions of the ISS cabin atmosphere; packing a heritage bed housing with the newly selected sorbent and conducting pressure drop testing; and integrating the bed into the exploration chamber (E-chamber) in parallel with the condensing heat exchanger and a metering bypass valve.

Actual progress for the fixed bed included successful completion of all planned tasks. Examining earlier NH_3 -targeting sorbent testing conducted at Ames Research Center (ARC) by Luna et al.,¹ Molecular Products Chemsorb[®] 1425 was chosen as the replacement for Barnebey-Sutcliffe Type 3032. Analysis of the fixed bed contaminant capacity was performed assuming that the adsorption equations defined for Barnebey-Sutcliffe Type 3032 applied to Chemsorb 1425. Pressure drop testing was conducted on the packed bed, and the bed was integrated into the E-chamber in parallel with the condensing heat exchanger and a metering bypass valve.

Results from the fixed bed analysis indicated that the bed should last 136 days before saturating with methanol, the most demanding compound considered in the analysis after carbon monoxide (CO), hydrogen, methane, and formaldehyde, all of which are readily oxidized in the catalytic reactor.

The Chemsorb 1425 that was ordered for testing unexpectedly arrived in mesh sizes 12×20 , much finer than the Barnebey-Sutcliffe Type 3032 at 4×8 . As a result, pressure drop through the bed was much higher than anticipated, and the bed could only reach a maximum flow rate of 5 cfm with the assistance of a blower.

The placement of the fixed bed in the E-chamber, in parallel with the condensing heat exchanger, enables direct comparison of the Chemsorb 1425's performance with the Barnebey-Sutcliffe Type 3032 since both the TCCS CBA and the fixed bed ingest cabin air at standard humidity; additionally, the placement of the fixed bed in parallel with a metering bypass valve allows for testing of the bed at various flow rates.

2.2 High-Temperature Catalytic Oxidizer

Planned progress for the HTCO using Microlith reactor technology included removing the unit from an old test fixture in the vacuum chamber (V-chamber), verifying unit functionality, determining optimal system placement in the overall E-chamber architecture, and integrating the unit into the E-chamber for cycle 1 testing.

Actual progress for the HTCO included successful completion of all planned tasks. The unit in the V-chamber was removed from the old test fixture and confirmed to be operational. Optimal placement for the HTCO was determined to be downstream of the carbon dioxide removal assembly (CDRA) zeolite 5A beds in the cabin air return flow path. At this particular location in the E-chamber architecture, the gas stream is very dry, reducing the heating burden on the HTCO heaters. The HTCO was then installed in the E-chamber in advance of cycle 1 testing.

Results from preliminary operational data for the HTCO Microlith unit indicate that the thermocouples within the unit are improperly labeled; this has yielded unexpected results in both the reactor's thermal cycling and in the thermal response time. Examination of the data led to selection of a different thermocouple for control of the unit's heaters, and system behavior is expected to return to nominal.

2.3 Orion Trace Contaminant Control Bed

For the Orion TCC bed, planned progress included designing a bed sized for the Orion cabin atmosphere, approximating the design with available legacy hardware, determining optimal bed placement in the E-chamber architecture, and integrating the bed into the E-chamber.

Actual progress for the Orion TCC bed yielded successful completion of all planned tasks. Published contaminant generation rates for both metabolic processes and equipment offgassing were coupled with projected Orion crew size and estimated equipment manifest to create a projected Orion cumulative contaminant load. The TCC bed was sized assuming a 30-day mission, and that the cabin atmosphere must be controlled to the 30-day spacecraft maximum allowable concentration for each published contaminant.

Once the bed was sized, heritage sorbent bed hardware was packed with a sorbent, Chemisorb 1425, and an ambient temperature CO catalyst, Carulite[®] 300. Optimal bed location was determined to be downstream of the CDRA zeolite 5A beds in the cabin air return flow path, upstream of the HTCO. This particular placement provides protection to the HTCO from any NH₃ that bypassed the fixed bed prior to CDRA; furthermore, it provides a very dry operating environment for the Carulite 300, which requires low humidity to function.

Results from the Orion TCC bed are forthcoming, as the E-chamber is not yet operating with contaminant injection capability.

2.4 Heat Melt Compactor Contaminant Control System

Planned progress for the HMC CCS included calculating an estimated total contaminant load emitted by the compactor for a 1-yr mission, evaluating potential control technologies against the quantity and composition of the contaminant load, making a recommendation to the HMC project, and delivering a report capturing all data and calculations supporting the recommendation.

Actual progress for the HMC CCS bed accomplished all planned tasks. ARC provided preliminary effluent data from a test run of the HMC unit at ARC. The data included probable contaminants present in the effluent, gas chromatograph mass spectrometer (GCMS) peak heights for the probable contaminants, and bulk contaminant concentration values. Listed probable contaminants were assumed to be present, recorded peak heights were assumed to uniformly relate to compound concentration, and the bulk contaminant emission plot was assumed to be symmetrical about the period of greatest emission. On the basis of those assumptions, contaminant load data were generated for a 1-yr mission, assuming the HMC would operate daily.

Two technologies were considered to treat the load: (1) A sorbent bed of activated carbon and (2) thermal catalytic oxidation. The sorbent bed analysis examined the performance of a treated activated carbon and an untreated activated carbon: Chemsorb 1425 and Chemsorb 1000, respectively. The second technology, thermal catalytic oxidation, was analyzed using data from previous HTCO Microlith testing and extrapolated ISS-scale system performance to the lower flow rates required for the HMC. Upon completion of the technology evaluation, the HMC project was advised to pursue a sorbent bed design filled with Chemsorb 1425.

Data and calculations used to support the recommendation were captured in a report entitled “Estimated Characteristics of a Trace Contaminant Control System for the Heat Melt Compactor,” completed in June 2012.² Data and conclusions from the report were presented at the HMC Preliminary Design Review in August 2012. Also, a contract was initiated with PCI to begin design of a Microlith catalytic reactor sized for the HMC in the event that further compactor effluent analysis should indicate catalytic oxidation is necessary.

Results from the initial HMC effluent analysis determined that the five predominant contaminants were acetoin, ethyl acetate, benzaldehyde, hexanal, and 3-methyl-1-butanol. Assuming GCMS peak magnitude directly correlated to contaminant concentration, the relative presence of each contaminant was found to be approximately 53%, 19%, 16%, 7%, and 5%, respectively, of the bulk contaminant concentration.

Results from the treatment technology evaluation showed that while untreated carbon required less sorbent mass to process the full load, the treated carbon provided additional capability as a means of NH_3 removal in the event of NH_3 generation in the HMC. Furthermore, the increase in required sorbent mass over untreated activated carbon was marginal at less than 50 g. Results from the Microlith catalytic reactor analysis projected that a unit sized for the HMC would likely achieve 97% oxidation efficiency at 90 W power consumption and would likely require 10 min to achieve light-off, or initiation of oxidation.

Given the catalytic oxidizer's significant power requirements compared to the unpowered sorbent bed, and the greater capability of the treated activated carbon over the untreated activated carbon, a sorbent bed packed with treated activated carbon was recommended. Such a configuration provided capability to remove NH_3 and other contaminants from the effluent stream while avoiding any additional power requirements.

The trace contaminant load and its variation will be characterized during FY 2013, and the catalytic oxidizer's design will be revisited based on that characterization. Fabrication is planned for late FY 2013 and early FY 2014.

3. FUTURE WORK

In the next few years, ARREM work for the TCC task will continue to advance NASA's airborne contaminant mitigation capabilities. Work in the next fiscal year will involve a variety of technologies and systems, including an Orion TCC bed, a high flow rate activated carbon system, an Orion smoke eater, a photocatalytic oxidation (PCO) system, and sorbent and catalyst testing and evaluation.

3.1 Orion Trace Contaminant Control Bed

The Orion TCC bed will compare directly to the system that is currently planned for the Orion vehicle. The bed design will employ multiple layers of sorbents and catalysts to effectively control the concentration of trace contaminants in the Orion cabin atmosphere. Myriad sorbent and catalyst evaluations will be performed to determine suitable candidates for inclusion in the Orion TCC bed.

3.2 High Flow Rate Carbon Bed

The high flow rate activated carbon system will be evaluated against the current ISS paradigm of treating a small flow rate with very high single-pass efficiency. By contrast to the ISS TCCS, a high flow rate activated carbon system will process cabin air at greatly elevated flow rates, though at a lower single-pass efficiency. The high flow capacity of the system will permit its possible incorporation into the ISS ductwork, eliminating requirements for a dedicated blower and potentially decreasing the volatile organic compound (VOC) burden for which the water recovery system is responsible.

3.3 Orion Smoke Eater

The Orion smoke eater will be designed to operate in the event of an Orion cabin fire, extracting particulates and chemical contaminants from the cabin atmosphere at a much higher rate than would be possible with the standard Orion TCC bed. The bed will employ multiple layers of sorbents and catalysts specially selected to target the products of combustion, such as CO.

3.4 Photocatalytic Oxidation System

PCO technology is a direct competitor with HTCO, the technology currently in use aboard the ISS. Both processes oxidize low molecular weight compounds across a variety of chemical classes and are used in conjunction with adsorption beds for TCC systems, as low molecular weight compounds are not readily adsorbed. The benefit of PCO technology is ambient temperature operation; by contrast, HTCO requires significant power input to reach operating temperatures above 300 °C and can even generate contaminants in the presence of certain compounds. PCO technology assessment will be conducted at Kennedy Space Center (KSC).

3.5 Sorbent Testing and Evaluation

Sorbents and catalysts will continue to be evaluated at KSC in support of various TCCS development efforts. As media are identified for potential integration into a TCCS, KSC personnel will assess media performance using an assortment of challenge compounds that represent particular metabolic or equipment offgassing loads. Data from KSC testing will guide sorbent and catalyst selection throughout system development.

APPENDIX A—BENCH-SCALE CHARACTERIZATION OF CANDIDATE SORBENTS AND CATALYSTS (TRACE CONTAMINANT CONTROL: CARBON DIOXIDE AND WATER REMOVAL)

A.1 Overview—Candidate Sorbent and Catalyst Testing by Kennedy Space Center

Research Milestones

Two candidate sorbents and two catalysts were tested in FY 2012:

- Evaluate TCC by silicalite.
- Evaluate carbon dioxide (CO₂) and water (H₂O) removal by immobilized amines.
- Evaluate ethanol removal by low-temperature CO catalysts.
- Evaluate ethanol removal with Honeywell PCO catalysts.

A.2 Silicalite

Silicalites (HiSiv 1000 and HiSiv 3000) are sorbents manufactured by Universal Oil Products (UOP) Honeywell that do not adsorb much CO₂ at 0.6% CO₂ and continue to adsorb VOCs at high moisture contents because they are hydrophobic.

Research Goals

- Evaluate the adsorptive capacities of HiSiv 3000 for gas mixtures (ethanol-acetone-toluene and dichloromethane-xylene) with 70%–80% relative humidity and 7 and 23 °C, respectively.
- Evaluate the adsorptive capacities of HiSiv 1000 for gas mixtures (ethanol-acetone-toluene and dichloromethane-xylene) with 70%–80% relative humidity and 7 and 23 °C, respectively.
- Measure adsorptive capacity data (umol/g) for calculating the size of single-pass silicalite beds.

Equipment

- Simulated cabin air gas streams (humidified gas mixtures) were supplied to 5 g of silicalite in the 0.5-in-diameter heated sorbent bed of the regenerable volatile organic compound control system (RVCS) testbed.
- Gas mixture analysis conducted using Fourier transform infrared (FTIR) spectrometer.

Procedures

- The UOP silicalites were loaded with VOCs at 1.5 SLPM in the 0.5-in-diameter RVCS bed.
- The silicalites were regenerated before use with reverse flow of nitrogen (N₂) and thermal ramping up to 260 °C for ≈4 hr.
- The tests were run for 3 hr to ensure maximum adsorption was reached.

Key Results

- HiSiv 3000 did not adsorb xylene, and absorption capacities followed acetone >> toluene > ethanol > dichloromethane. HiSiv 3000 was dusty after removal from the bed.
- HiSiv 1000 adsorption was acetone >>> ethanol >> toluene > xylene/dichloromethane. More toluene was adsorbed when dry. Dichloromethane showed rollover with water vapor. HiSiv 1000 was not dusty after removal from the bed.
- A data summary was sent to Marshall Space Flight Center (MSFC) in February as requested.
- Additional silicalite characterization was not possible due to flooding of the Space Life Sciences Lab.

A.3 Immobilized Amines (G10 and Polyethyleneimine-Silane)

CO₂ adsorptive capacities of immobilized amines (G10 and polyethyleneimine- (PEI-) silane), synthesized by the National Energy Technology Laboratory (NETL), were evaluated at various loading temperatures.

Research Goals

- Measure breakthrough curves for CO₂ adsorption of G10 at 20, 40, and 60 °C using low flow rates.
- Measure breakthrough curves for CO₂ adsorption of PEI-silane at 20, 40, and 80 °C using low flow rates.
- Study the effect of humidity on the CO₂ adsorption of G10.

Equipment

- Simulated cabin air gas streams (0.6% CO₂) were supplied to 5 g of immobilized amines in the 0.5-in-diameter heated sorbent bed of the RVCS testbed.
- Gas mixture analysis conducted using FTIR spectrometer.

Procedures

- The immobilized amines were loaded with CO₂ at 0.5 SLPM in the 0.5-in-diameter RVCS bed.
- The immobilized amines were regenerated before use with reverse flow of N₂ at 100 °C for 1 hr.

Key Results

- The data collected were sent to the University of South Carolina to corroborate their modeling efforts at explaining mechanisms of CO₂ absorption by these immobilized amines.
- The data were shared with NETL and MSFC to evaluate the possible use of these immobilized amines as substitutes for SA9T.

A.4 Low-Temperature Carbon Monoxide Catalysts

Research Goals

- Evaluate low-temperature CO catalysts for removal of VOCs.
- Two gold-based commercial catalysts (TDA Research, Inc. and Novax Material and Technology Co.) and one platinum- (Pt-) tin, oxide-based catalyst were studied.

Equipment

- Simulated cabin air gas stream (humidified ethanol).
- Gas mixture analysis conducted using a gas chromatograph (GC) and an FTIR spectrometer.

Procedures

- VOCs were tested over oxidation catalysts to determine the conversion rates. The catalysts were exposed to ethanol at concentrations less than 20 ppm and at a flow rate of 0.6 SLPM. Maximum allowable concentration limit for ethanol is 1,000 ppm in an enclosed space. VOCs vent into a carbon filter.
- Three catalysts were tested. Catalysts prepared by TDA Research, Inc. and Novax Material and Technology Co. are gold-based catalysts; the third one is a Pt-tin-oxide catalyst.
- Ethanol was generated with an impinger. Nitrogen gas flows through a flow meter into 15 mL of ethanol and generates a gas stream of 20 ppm of VOCs that flows at 0.6 SLPM through 20–50 mg of catalyst. The ethanol concentrations were sampled before and after the tube containing the catalyst.
- The gas samples were analyzed with a GC and FTIR. Catalyst samples, used and new, were analyzed with x-ray photoelectron spectroscopy (XPS).

Key Results

- Studied all three catalysts, but TDA performed the best. No intermediates were formed and it lasted longer.
- Ethanol thermocatalytic removal using a gold/iron-oxide (TDA Research) catalyst at room temperature (TDA Research catalyst was previously tested at ARC for low-temperature CO oxidation). Initial ethanol removal was rapid for the first 2–3 hr followed by saturation/poisoning of the catalyst. Figure 1 shows that the XPS analysis of the carbon region before (fig. 1(a)) and after (fig. 1(b)) indicates formation of carbonyl species on the surface of the catalyst with a reduced concentration CO indicative of a surface reaction with no ethanol absorption.

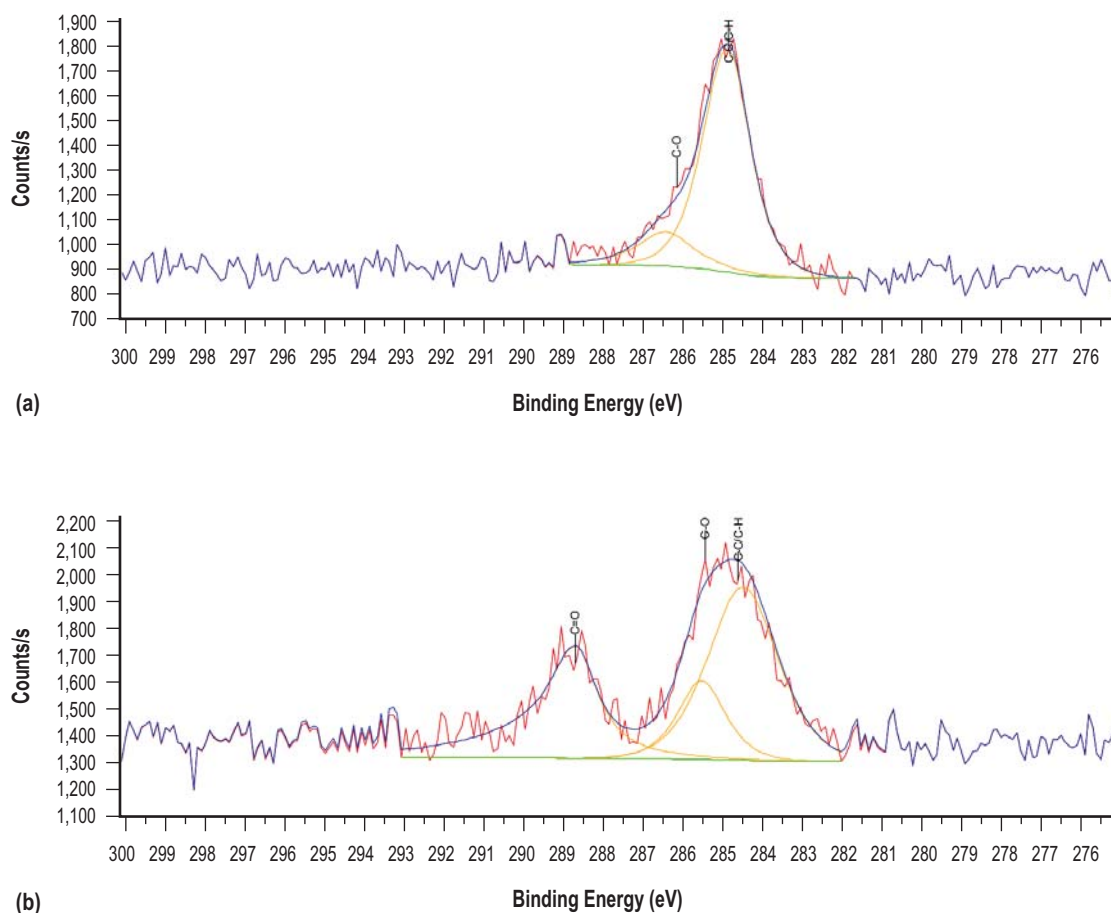


Figure 1. XPS analysis of TDA Research catalyst before and after an ethanol challenge: (a) New and (b) used.

A.5 Honeywell Photocatalyst Evaluation

A collaborative effort was initiated with Honeywell regarding the manufacture of doped photocatalyst coupons for testing at KSC (table 1). The effort has been slow, tedious, and ongoing. Testing was not possible in FY 2012 as the catalyst coupons had not been delivered by Honeywell.

Research Goals

- Measure PCO degradation of ethanol and acetone using ultraviolet A (UV) (UVA) and ultraviolet C (UVC) radiation using Honeywell doped PCO catalyst coupons in the fast flow photocatalytic oxidation (FF PCO) of the Solar Simulator testbed.
- Measure PCO degradation of ethanol in presence of VOC mixtures.
- Study the effect of humidity PCO degradation of ethanol.

Table 1. Event timeline for Honeywell PCO catalyst testing.

Date	Purpose	Document
4/2011	Contacted Honeywell with collaborative ideas	AVO_Ideas_ARSystems
11/2011	Established NDA with Honeywell	NDA
5/2012	Suggested test plan of Honeywell catalysts	Test Plan
8/2012	Requested quote for coupon fabrication	Informal request
9/2012	Awaiting quote for Honeywell catalyst coupons	–

Equipment

- Vacuum-sealed, ultraviolet- (UV-) irradiated, FF PCO reactor bed.
- Simulated cabin air gas stream supplied to the FF PCO bed in the RVCS testbed.
- Gas mixture analysis conducted using FTIR spectrometer.
- UVA and UVC supplied by the Solar Simulator Testbed.

Procedures

- Honeywell catalyst would be regenerated by vacuum desorption for 1 hr during UVC irradiation.
- Load Honeywell catalyst with a known amount of ethanol and irradiated by UV in a closed-loop photocatalytic reactor.
- Rates of intermediate formation during PCO will be measured using FTIR as a function of moisture present in the gas stream.
- The effects of toluene and xylene on intermediate formation will be studied.

APPENDIX B—BENCH-SCALE DEVELOPMENT OF A CATALYST FOR SELECTIVE CONVERSION OF AMMONIA TO NITROGEN

B.1 Summary

Research Goals

- Demonstrate that NH_3 (2–5 ppm) from spacecraft cabin gas streams can be converted to N_2 using selective catalytic oxidation (SCO).
- Develop a low-temperature, platinum-based catalyst (LTP catalyst) for SCO.
- Demonstrate that LTP catalyst reduces the temperature required for NH_3 removal.
- Demonstrate that LTP catalyst does not produce toxic nitrogen oxides (NO_x) (nitric oxide (NO) and nitrogen dioxide (NO_2)) and reduces nitrous oxide (N_2O) formation.
- Study the effect of water vapor and temperature on NH_3 removal from spacecraft gas streams using SCO.

Equipment

- Gas mixture analysis was conducted using FTIR spectrometry in the RVCS testbed. The RVCS was modified by adding a 66-L semisealed chamber.
- Permeation tubes for the gas generator were expensive and could not supply enough NH_3 , thus a custom NH_3 generator was designed, tested, and implemented.
- The LTP catalyst was contained within the 0.5-in-diameter bed of the RVCS. Bed temperatures were controlled between 23 and 220 °C. The fine powder was contained using 100 mesh screens.

Procedures

- The LTP catalyst was synthesized at the Air Revitalization Lab, KSC.
- The RVCS was configured to run in closed-loop mode to measure NH_3 removal rate and NO , N_2O , and NO_2 production using several LTP catalyst formulations at various temperatures.
- The NH_3 generator was used to supply 17 ppm and 450 ppm NH_3 to 66 L of air recirculated through 3.2 g of LTP catalyst contained in the heated RVCS sorbent bed.

Key Results

- ARREM-funded FY 2012 work at KSC developed LTP catalyst that oxidizes NH_3 into N_2 and only produces trace amounts of N_2O at 150 °C. The ability of the LTP catalyst to remove NH_3 from cabin air at low temperatures (150 °C) was demonstrated.
- The LTP catalyst is a fine powder that causes a large pressure drop when used in a catalyst bed.
- The LTP catalyst powder is also hard to contain within the catalyst bed volume as it passes through 50–100 mesh screens.

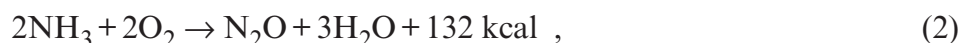
B.2 Synthesis of a Low-Temperature, Platinum-Based Catalyst for Ammonia Removal

B.2.1 Overview

Air revitalization technologies maintain a safe atmosphere inside spacecraft by the removal of CO₂, NH₃, and trace contaminants. NH₃ onboard the ISS is produced by crew metabolism, payloads, or accidental release of thermal control refrigerant. TCC onboard the ISS is accomplished not only by the TCCS, but also by other Environmental Control and Life Support System subassemblies. These additional removal routes include absorption by humidity condensate in the temperature and humidity control condensing heat exchanger and adsorption by the CDRA.

Currently, the ISS relies on removing NH₃ via humidity condensate and hooded respirators (during emergencies). A better approach to cabin NH₃ removal is SCO because it builds on existing thermal catalytic oxidation concepts that have flight experience and could be more readily incorporated into the existing TCCS process equipment architecture on the ISS.

SCO of NH₃ is carried out via the mechanism shown in equations (1)–(3):



and



At low temperatures (<500 °C), all three N₂-containing products (N₂, N₂O, and NO) are formed simultaneously in various proportions in the presence of many catalysts. The challenge of implementing SCO is to reduce formation of undesirable byproducts like NO_x (N₂O and NO).

An LTP catalyst was developed at KSC in FY 2012 for converting NH₃ to H₂O and N₂ gas by SCO. This SCO catalyst could significantly reduce the upstream sorbent bed size of TCCS to address only organo-silicone compounds, which currently also adsorbs NH₃.

B.2.2 Low-Temperature, Platinum-Based Catalyst Synthesis

The LTP catalyst (fig. 2) was synthesized by doping ZSM-5 with diamine-Pt-nitrite. The Pt was doped using various impregnation methods. After impregnation, the LTP catalyst was dried at 120 °C overnight and calcined at 500 °C for 6 hr in a muffle furnace.

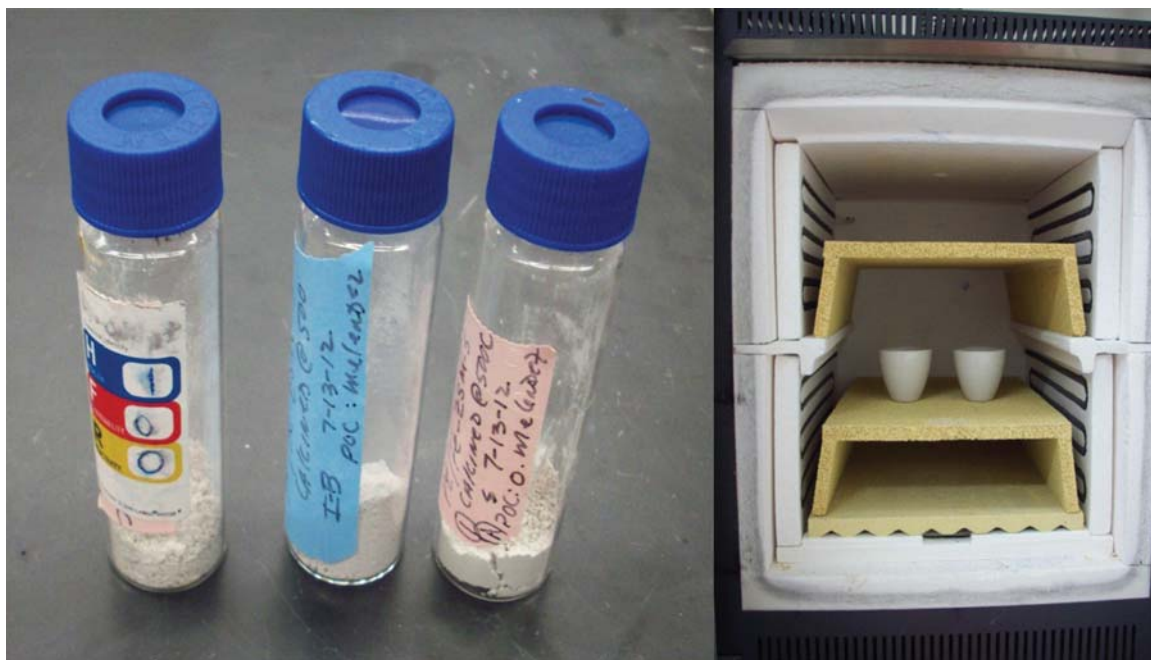


Figure 2. LTP catalyst samples.

B.3 Study of Ammonia Removal Using Closed-Loop Fourier Transform Infrared Spectrometer

B.3.1 Regenerable Volatile Organic Compound Control System Modifications

The RVCS testbed (fig. 3) was modified by adding a 66-L semisealed chamber and an NH_3 generator. The RVCS was reconfigured in a closed-loop mode to test the SCO NH_3 removal rate using the LTP catalyst. An NH_3 generator was devised to supply NH_3 concentrations ranging from 1 to 700 ppm to a 66-L chamber. A pump recirculates chamber air among the chamber, FTIR, and catalyst bed. The FTIR measures NH_3 , NO , N_2O , and NO_2 production during SCO.

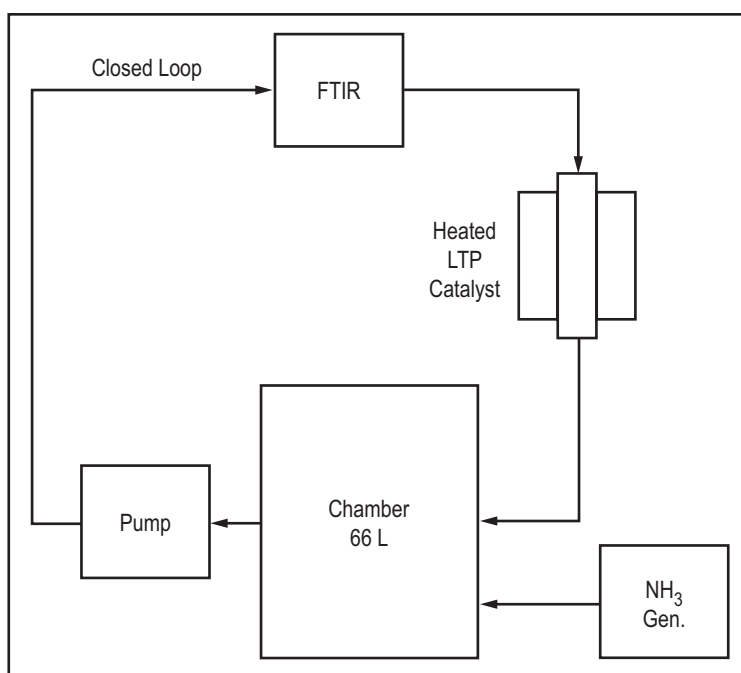


Figure 3. RVCS block diagram.

B.3.2 Ammonia Generation Methods

NH_3 permeation tubes for the KIN-TEKTM gas generator of the RVCS were expensive and could not supply enough NH_3 , thus a custom NH_3 generator was designed, tested, and implemented. NH_3 was generated by supplying ammonium chloride (NH_4Cl) solutions of known molarity onto excess sodium hydroxide (NaOH) pellets. NH_3 is released into a 2-L NH_3 generator (fig. 4) as an NH_4Cl solution is delivered to NaOH pellets via syringe. NO_2 was found to be generated via this procedure. The NH_3 generated in the NH_3 generator can be swept into the 66-L chamber as needed to bring the NH_3 concentration in the chamber to the same initial concentration.

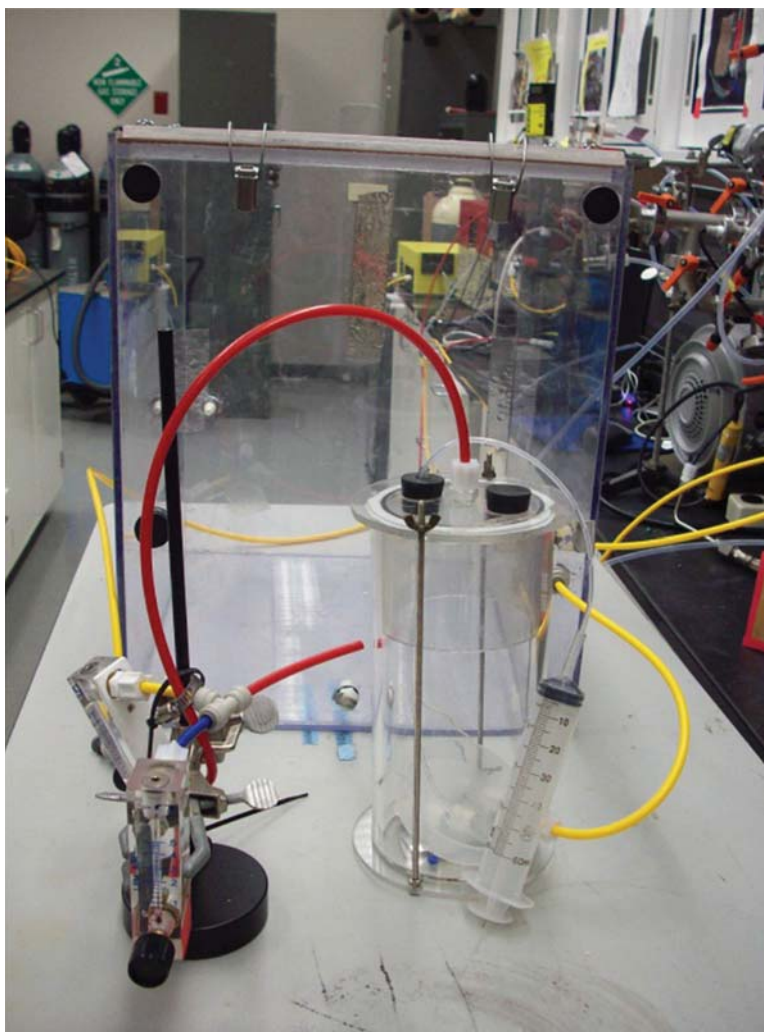


Figure 4. Custom gaseous NH_3 generator.

B.4 Low-Temperature, Platinum-Based Catalyst Testing

B.4.1 Platinum Content

The amount of Pt dopant was varied, and the amount of NO produced at 165 °C was found to increase as the amount of Pt was decreased.

B.4.2 Chamber Gas Composition—Ammonia Removal Experiment

The 66-L chamber was filled with lab air, which contains atmospheric NO, and with water vapor. Initially, the gas was recirculated bypassing the catalyst bed. Then, the gas was mixed with NH₃ generated in the NH₃ generator (fig. 5), and NH₃ concentration (right axis) rose up to 18 ppm after 1 hr. The gas generator introduced up to 0.1 ppm of NO and NO₂. The chamber was then recirculated, bypassing the bed, and the concentration of most gases (NH₃, CO₂, NO, and NO₂) decreased at the chamber leak rate. At 1.8 hr, the gas generator increased the NH₃ concentration, and the air was circulated through the LTP catalyst bed. At 3.2 hr, the NH₃ was increased again and allowed to flow through the bed. NH₃ was added to the 66-L chamber with the NH₃ generator and leak rate measured in the first 1.7 hr. NH₃ removal by the LTP catalyst was measured after 1.7 hr.

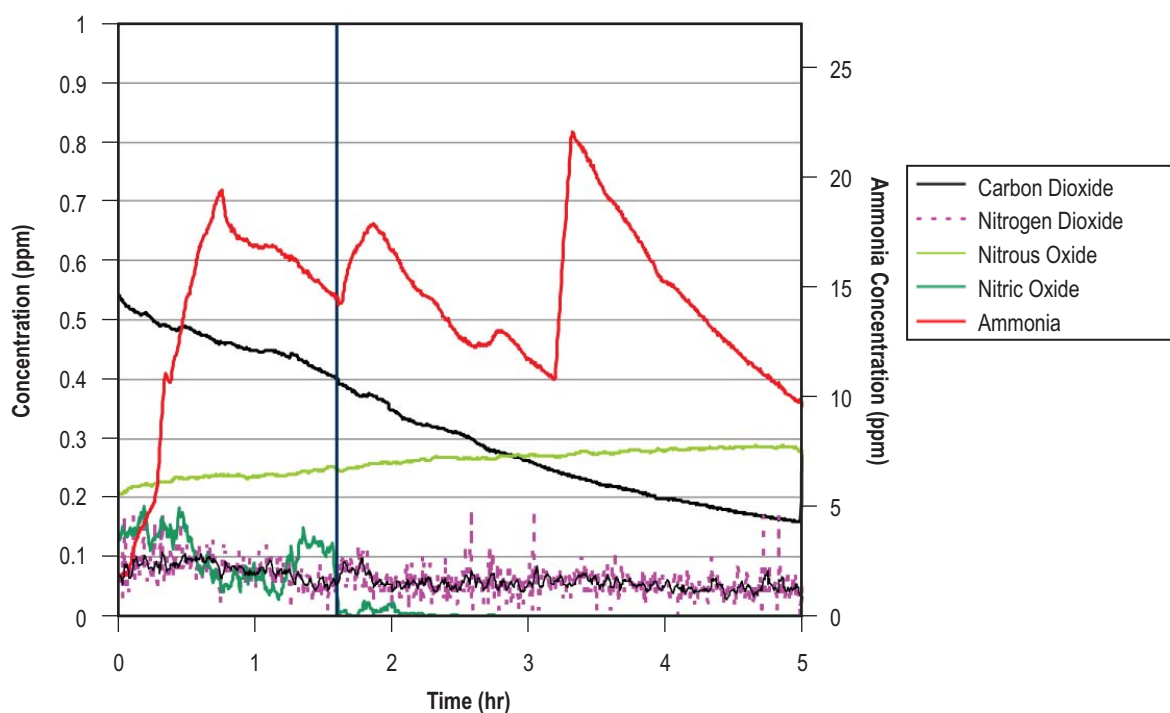


Figure 5. RVCS chamber NH₃ concentration dynamic.

B.4.3 Chamber Leak Rates

The 66-L chamber was found to be leaky, thus its leak rate had to be determined in order to accurately determine NH_3 removal rates. NH_3 concentration in the chamber (C_{ch}) will decrease due to a concentration gradient to a lower external concentration (C_{ext}). The chamber leak rate was determined by fitting NH_3 concentration data to equation (4):

$$\text{Leak (\%/hr)} = (100/\Delta t) \times \ln((C_{ch1} - C_{ext1}) / (C_{ch2} - C_{ext2})) \quad (4)$$

NH_3 concentration in the 66-L chamber decreased when the LTP catalyst bed was not present due to the chamber leak rate. The NH_3 removal obtained from changes in chamber concentration must be corrected for the leak rate. The chamber leak rate (fig. 6) was found to be 30%–33%/hr, and it was sensitive to the recirculating flow rate of the closed-loop system. The chamber leak rate was also confirmed by using changes in chamber CO_2 concentration.

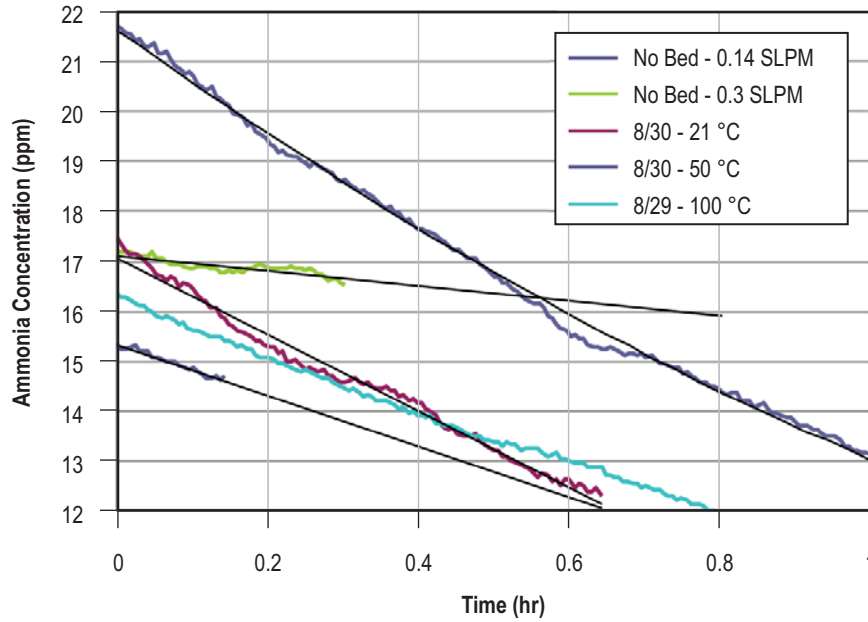


Figure 6. RVCS chamber NH_3 concentration decay profile.

B.4.4 Ammonia Removal Versus Ammonia Concentration

The NH_3 removal rate corrected for chamber leak rate ($r\text{NH}_3$) was determined at 150 °C and 1.4% water vapor using two NH_3 concentrations (table 2). The $r\text{NH}_3$ was 3.3 mg/g/hr at 17 ppm and rose to 53 mg/g/hr. The NH_3 removal rates for a 500-g bed of LTP catalyst at 150 °C were 1.7 g/hr and 27 g/hr at 17 ppm and 420 ppm, respectively. N_2O concentration in the 66-L chamber increased dramatically as the LTP catalyst bed temperature exceeded 170 °C.

Table 2. NH_3 removal rate corrected for RVCS chamber leakage.

Ammonia Concentration (ppm)	Chamber Leak Rate (mg/g/hr)	Bed Removal Rate (g/hr)
17	3.3	1.7
420	53	27

B.4.5 Temperature Effects

The N_2O concentration in the 66-L chamber was 0.35 ppm from a catalyst bed temperature of 20 to 150 °C (fig. 7). N_2O concentration in the 66-L chamber increased dramatically as the LTP catalyst bed temperature exceeded 170 °C. It rose to 0.47 ppm at 170 °C and was 1.8 ppm at 200 °C. Nitric oxide and NO_2 formation was not detected during NH_3 removal via SCO with the LTP catalyst.

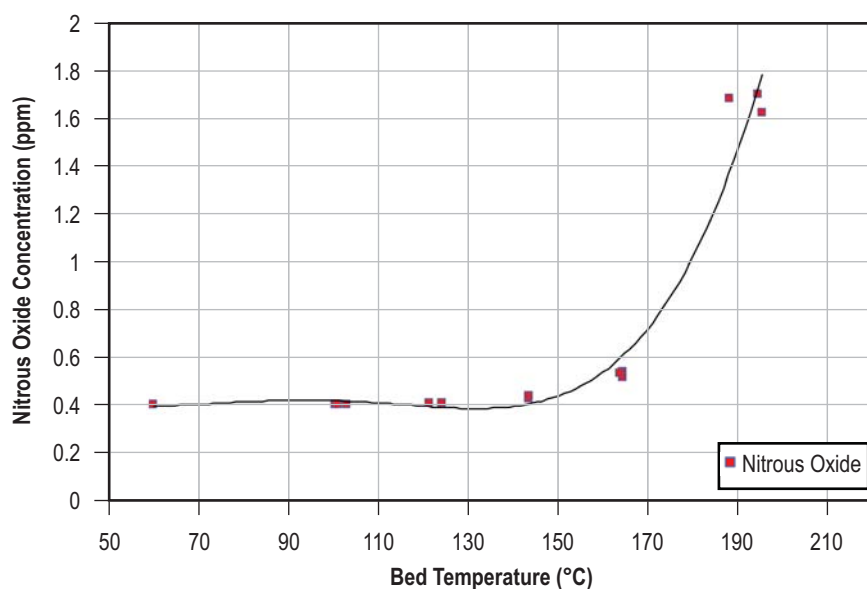


Figure 7. Temperature influence on N_2O concentration in the RVCS chamber.

B.4.6 Pressure Drop

The bed containing 3 g of LTP catalyst decreased the flow rate through it by 50%. The talcum powder consistency of the LTP catalyst resulted in a large pressure drop. It was also hard to contain with 100 mesh screens. The powder was found outside the bed on several occasions.

B.5 Future Development of Low-Temperature, Platinum-Based Catalyst

B.5.1 Microlith Development

The LTP catalyst is a fine powder, which leads to high pressure drop and poor containment. Future work should aim to reduce pressure drop and improve reliability. PCI was contacted for exploring the possibility of coating the LTP catalyst onto Microlith metal mesh elements. A non-disclosure agreement was established with PCI, and they submitted a statement of work. This work is being proposed as a KSC Center Investment Fund proposal. The current Technological Readiness Level (TRL) of the LTP catalyst is 2. The expected TRL after incorporating it onto Microlith is 3.

REFERENCES

1. Luna, B.; Somi, G.; Winchester, J.P.; et al.: “Evaluation of Commercial Off-the-Shelf Sorbents and Catalysts for Control of Ammonia and Carbon Monoxide,” Paper Presented at AIAA 2010, 40th International Conference on Environmental Systems, Barcelona, Spain, July 11–15, 2010.
2. Pruitt, M.W.; and Perry, J.L.: “Estimated Characteristics of a Trace Contaminant Control System for the Heat Melt Compactor,” NASA Marshall Space Flight Center, AL, 12 pp., June 2012.

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